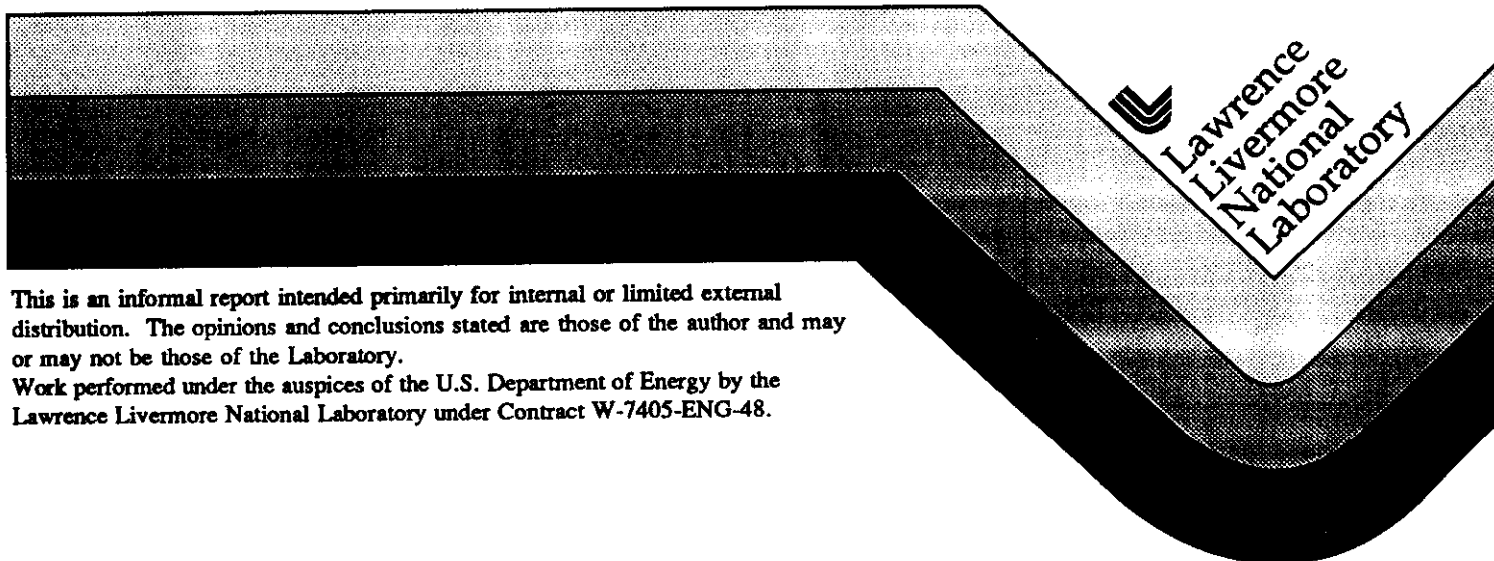


Selenium Isotope Geochemistry: A New Approach to Characterizing the Environmental Chemistry of Selenium

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Selenium Isotope Geochemistry: A New Approach to Characterizing the Environmental Chemistry of Selenium

Authors: Alan M. Volpe and Bradley K. Esser

High levels of selenium in the environment will be a prominent water quality issue in the western United States for many years. Selenium accumulation is linked to increased rates of death and deformity in migratory birds, blind staggers in domestic livestock, and selenosis in humans. In California, agricultural drain waters (e.g., Kesterson) and oil refinery effluent (e.g., Unocal) contribute to high selenium content in the San Joaquin Valley and the San Francisco Bay. The importance of these industries to California's economy precludes simple abatement, while the complexity of selenium cycling precludes simple remediation.

The purpose of this project is to measure variations in the isotopic composition of selenium in water and soil samples caused by natural processes and to show, for the first time, the value of isotopic measurements in characterizing selenium pollution. The research seeks to identify sources of selenium pollution, determine processes in the selenium cycle, and support selenium remediation studies. The project required the successful integration of three components: 1) appropriate sampling a field setting showing Se enrichment and possibly isotopic fractionation, 2) analytical chemical methods for isolating and purifying the various species of Se in waters and sediment, and 3) mass spectroscopic instrumentation for high precision isotope abundance measurements.

During FY95 we developed chemistry to extract and purify the various species of selenium found in waters and soils. We use an anion-exchange column chemistry that allows us to pre-concentrate, separate, and determine low levels of different selenium species (selenite, selenate, and reduced selenium) in natural waters. Development of this technique involved the preparation of standards and enriched isotope solutions, which will be useful in isotope dilution and isotopic composition work. Figure 1 shows typical separation using anion resin column. The ability to separate the naturally occurring species of selenium is critical to understand selenium isotope fractionation.

In May 1995, we sampled waters from natural springs and creeks in the Panoche Hills on the western side of San Joaquin Valley. These sulfur-rich waters are a significant source of natural selenium from marine shales that form the Coast Range mountains. Table 1 shows selenium data for Panoche Hills water. Selenium contents range from 3 to 50 parts-per-billion, considerably enriched over typical river abundances of 0.02 to 0.70 ppb. The water from Silver Creek is selenite-rich with Se-IV/Se-VI close to 0.75. Field sampling was planned the following year to collect sediment and water samples from agricultural ponds in the San Joaquin Valley and tidal marshes in North San Francisco Bay. We

hypothesize that microbially mediated reduction processes in sediments will affect both the speciation and isotopic composition of selenium in natural and contaminated systems.

The main effort the second year, FY96, involved conversion of an existing mass spectrometer from positive ion to negative ion measurement capability. This project successfully provided a new analytical capability for LLNL isotopic analysis, negative thermal ionization mass spectrometry (NTIMS). Upon completion of software and hardware modifications, we measured selenium isotopic composition with high precision and accuracy in seventy samples using the enhanced instrument. Table 2 shows results completed the last half of FY96. Samples were selected to study ionization efficiency, instrumental isotopic fractionation, ion beam stability for different species of Se measured as standard solutions and standards processed through chemistry. Precision and accuracy of the isotope measurements are excellent; better than 0.3% for the minor isotope (^{74}Se) and better than 0.05% for the major isotope (^{80}Se). This level of precision is sufficient to characterize selenium isotopic fractionation in nature, which is thought to occur at the percent level.

Repeated measurement of standard solutions of selenite and selenate processed through chemistry clearly demonstrates (Table 2) that reduction steps in our chemical procedures do not result in isotopic fractionation of selenium. Therefore, we are confident that our chemical procedures and measurement techniques are capable of determining whether or not natural processes lead to Se isotopic fractionation in the environment.

LDRD-ERD funding for the third year was not continued. Unfortunately, this occurred at the peak stage in the project when all three components necessary for successful demonstration of the Se isotope concept were complete. It is ironic that colleagues at LBL working on a parallel effort were the first to demonstrate recently (AGU Meeting, December 1996) the value of selenium isotopic study using NTIMS to environmental problems in the San Francisco Bay (Johnson et.al., EOS, v77, n46, pF216).

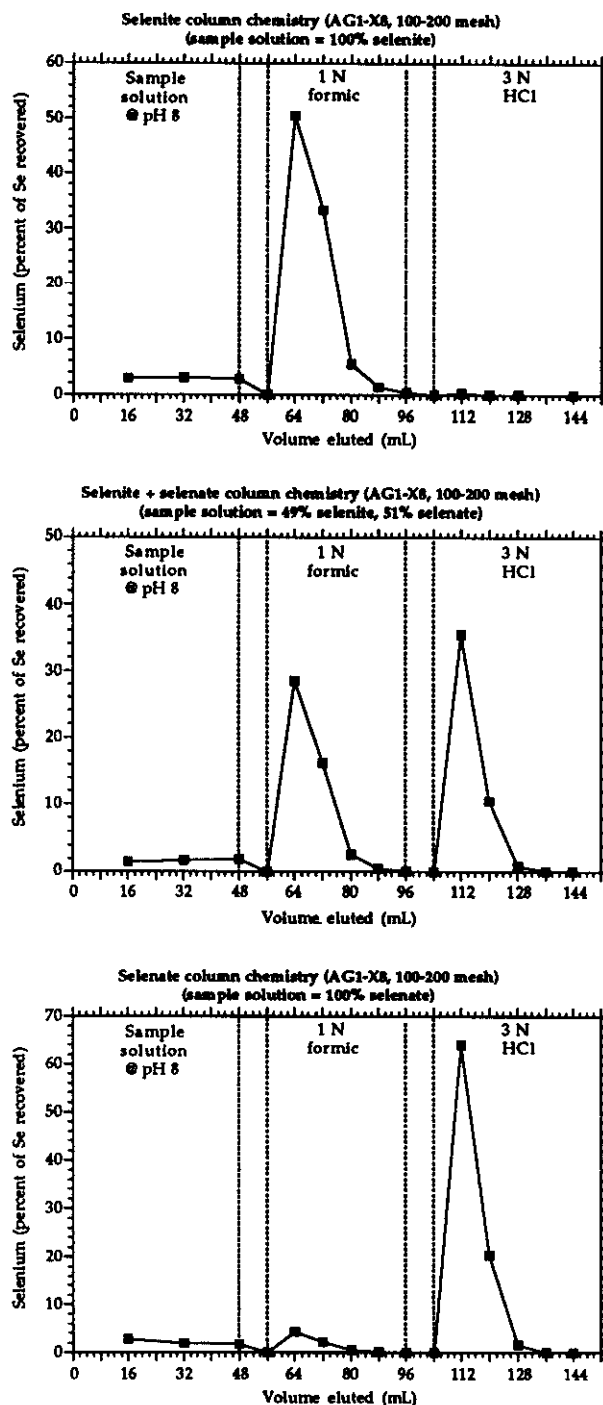


Figure 1. Selenite and selenate column chemistry on AG1-X8 anion exchange resin. This technique effectively separates selenite and selenate with high and reproducible chemical yield. For each of the three calibrations, ~50 mL of a standard solution containing selenite, selenate or a mixture of selenite and selenate was brought to pH 8 with KOH and passed through 2 mL of resin. Selenite was eluted in 1 N formic acid, while selenate was eluted in 3 N HCl. The column was rinsed with 8 mL of MQ water after the sample solution and after the formic acid. Column cuts were analyzed by ICPMS with better than 5% precision. The apparent breakthrough during loading of the sample solution (0–48 mL) is not real, it reflects interferences of K in the Se mass region during ICPMS analysis. The selenite signal in the selenate experiment (56–72 mL) reflects residual selenite in the selenate standard—this standard was prepared by oxidizing a selenite standard.

TABLE 1.

	T (°C)	pH	Conductivity (mS)	Alkalinity (ppm HCO ₃)	SeIV (ppb)	SeVI (ppb)	SeIV+VI (ppb)
Sulfur Seep @ Griswold Creek	19.9	6.75	8.4	600	4.5	44.4	48.9
Griwold Creek @ Sulfur Seep	24.0		4.5		1.5	11.4	12.9
Silver Creek @ Panoche Road	19.8	8.20	3.7	450	6.9	9.3	16.1
San Carlos Creek @ Kreyenhagen Boulder Seep	26.3	8.36	2.4	450	0.1	3.4	3.4
Kreyenhagen Boulder Seep @ San Carlos Creek	27.6	7.77	12.6	125	3.4	31.5	35.0

TABLE 2.

Se Samples for NTIMS					
Isotope Ratios*	⁷⁴ Se/ ⁸² Se 0.10182	⁷⁶ Se/ ⁸² Se 1.0727	⁷⁷ Se/ ⁸² Se 0.8745	⁷⁸ Se/ ⁸² Se 2.723	⁸⁰ Se/ ⁸² Se 5.6817
	Frac Corr	Frac Corr	Frac Corr	Raw	Frac Corr
Standard Solutions					
Selenium-IV: Loading technique A					
Mean (n=13) +/- 2σ	0.10140 0.00018	1.1432 0.0251	0.8807 0.0010	2.674 0.010	5.6722 0.0025
Selenium metal, dissolved in (HNO ₃) _c , oxidized to Se IV, Loading technique B					
Mean (n=8) +/- 2σ	0.10154 0.00014	1.1040 0.0081	0.8795 0.0006	2.667 0.014	5.6740 0.0019
Selenite SeO ₂ dissolved in dilute HNO ₃ , pH1-2, Loading technique B					
Mean (n=5) +/- 2σ	0.10149 0.00034	1.0963 0.0149	0.8770 0.0008	2.649 0.031	5.6781 0.0058
Spex ICP-MS standard, Selenium dissolved in 2% HNO ₃					
Mean (n=3) +/- 2σ	0.10159 0.00007	1.0951 0.0174	0.8777 0.0008	2.691 0.015	5.6785 0.0014
Selenium-IV: Loading technique B					
Mean (n=14) +/- 2σ	0.10144 0.00021	1.1154 0.0054	0.8796 0.0004	2.676 0.001	5.6747 0.0016
Column Chemistry Samples: Standard solutions through chemical separation and handling					
Selenite IV, selenium metal, chemistry (Heumann) KOH/formic acid					
Mean (n=7) +/- 2σ	0.10100 0.00026	1.1762 0.0207	0.8864 0.0019	2.702 0.014	5.6690 0.0010
Selenite IV, Se metal, oxidized to selenite, column chemistry (Heumann) NH ₄ OH/formic acid					
Mean (n=2) +/- 2σ	0.10197 0.00089	1.1841 0.0128	0.8872 0.0003	2.702 0.006	5.6723 0.0004
Selenate VI, Se metal, oxidized to selenate, column chemistry (Heumann) , reduced to selenite					
Mean (n=4) +/- 2σ	0.10130 0.00039	1.1769 0.0287	0.8838 0.0029	2.683 0.018	5.6639 0.0032
Selenate VI, Se metal, oxidized to selenate, no column chemistry, reduced to selenite					
Mean (n=2) +/- 2σ	0.10169 0.00028	1.1304 0.0225	0.8792 0.0002	2.679 0.018	5.6748 0.0017
Isotope abundances are from: Wachsmann & Heumann, 1992, International Journal Mass Spectrometry & Ion Processes, vol. 114, 209-220.					
Isotope ratios are fractionation corrected (FracCorr) using measured (Raw) ⁷⁸ Se/ ⁸² Se and normalization abundance ratio equal to 2.723.					